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(54) Title: SYNERGISTIC ALGAECIDE

(57) Abstract

This invention is directed to a broad spectrum algaecidal composition which comprises a mixture of a halopropynyl compound and zinc pyrithione, said mixture provided in an amount to prevent and/or protect a substrate, such as in industrial systems, from attack by one or more algael organisms.

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SYNERGISTIC ALGAECIDE

FIELD OF THE INVENTION

This invention is directed to a algaecidal composition and particularly a synergistic mixture or combination of zinc pyrithione and a halopropynyl compound.

BACKGROUND OF THE INVENTION

Both exterior and interior surfaces and substrates of all types, when exposed to common environmental conditions, e.g. moisture, are prone to attack, discoloration and various kinds of destruction by algael organisms. As a result, there is a great need and requirement for an effective and economical means to protect for extended periods of time both exterior and interior surfaces and various type substrates from the deterioration and destruction caused by such microorganisms.

Materials which need protection with a suitable antimicrobial composition for controlling algael microorganisms and their adverse effects include paints, coatings, stucco, concrete, stone, cementaceous surfaces, wood, caulking, sealants, and textiles as well as materials and other substances which may be attacked by algae.

Commercial products designed for the control of algae on such substrates are available. All of which, to

varying degrees, could retard or prevent the growth of and accompanying destruction caused by algae microorganisms. However, there is still a need in the art to develop more and better products to combat algae.

There are a number of organic compounds and especially certain carbamates, such as the halopropynyl or halopropargyl carbamates which are known primarily for their fungicidal activity. 3-iodo-2-propynyl butyl carbamate, hereinafter also referred to as IPBC, is a well known and highly active broad spectrum fungicide. In addition to its fungicidal activity, IPBC also has been associated with algaecidal activity. In this regard, Great Britain Patent 2,138,292 and U.S. Patents 4,915,909 and 5,082,722 contain such disclosures.

IPBC has been found to perform in a synergistic fashion with a variety of adjuvants. In particular, U.S. Patent 4,844,891 (with formaldehyde donors); U.S. Patent 5,128,372 (with N-4-dihydroxy-α-oxobenzene-ethanimidoyl chloride); U.S. Patent 5,134,158 (with 3,4-dichloro-1,2-dithiol-3-one); U.S. Patent 5,134,160 (with 2,2-dibromo-2-nitrilopropionamide); U.S. Patent 5,147,890 (with N,N-dimethyl-N'-phenyl-(N'- fluorodichloromethylthio) sulfamide); U.S. Patent 5,147,891 (with phenyl-(2-cyano-2-chlorovinyl) sulfone); U.S. Patent 5,162,343 (with sodium 2-pyridinethiol-1-oxide); U.S. Patent 5,219,875 (with 1,2-benzisothiazolon-3-one) and U.S. Patent 5,428,050 (with N-[1,3-bis(hydroxymethyl)-2,5-dioxo-4-imidazolidinyl]-N,N'-bis(hydroxymethyl) urea) each describe the use of IPBC in binary synergistic mixtures.

Japanese application 92-0197639 describes a composition containing IPBC and 2-octyl-isothiazoline-3-on as having improved anti-mold activity. Canadian 2,053,807 indicates that a certain range of proportions of 2-n-octyl-4-isothiazolin-3-one and IPBC exhibits synergy in controlling the growth of bacteria.

Zinc pyrithione is an algaecide and also a fungicide. It is a widely known successful anti-dandruff agent. It is described in U.S. Pat. No. 3,236,733 as an ecologically and physiologically safe substance which is added to shampoo in a simple manner. Zinc pyrithione can also be mixed with other anti-microbial agents such as TBZ (tiazolebenzimidazole) and PCMX (p-chloro-m-xylenol) into a silicon resin emulsion for a resin coat layer in a air passage changeover device. This is described in U.S. Pat. No. 5,326,315.

However, the synergistic effect obtained by combining a halopropynyl compound such as IPBC and zinc pyrithione has not been previously disclosed. The prior art has completely failed to appreciate any benefit from combining zinc pyrithione with a halopropynyl compound such as IPBC to obtain an unexpectedly high synergistic activity against algae.

BRIEF DESCRIPTION OF THE INVENTION

The present invention is based on the surprising synergistic effect that a combination of zinc pyrithione and a halopropynyl compound, and particularly a halopropynyl carbamate compound, has on the increased

efficacy of the resulting combination, especially against algae.

In accordance with a preferred embodiment of the invention, it has now been discovered that a synergistic combination containing in particular 3-iodo-2-propynyl butyl carbamate (IPBC) and zinc pyrithione gives a surprising and unexpected algaecidal effect. Relative proportions of the two components in compositions according to the present invention may be varied within relatively wide limits.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to a synergistic combination of a halopropynyl compound, particularly a halopropynyl carbamate such as IPBC, and zinc pyrithione.

A halopropynyl (halopropargyl) compound for use in the present invention can be identified by the following structure:

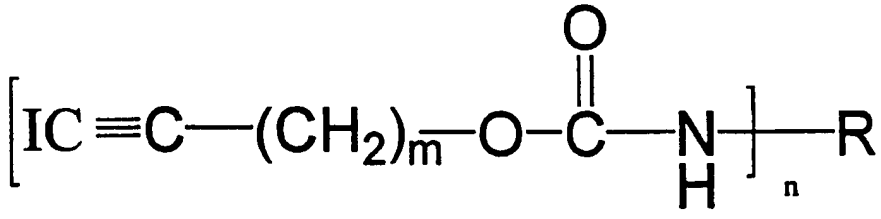
$$YC \equiv C - CH_2\ X$$

wherein Y is a halogen, preferably iodine and X can be (1) oxygen which is part of an organic functional group; (2) nitrogen which is an organic functional group; (3) sulfur which is part of an organic functional group; or (4) carbon which is part of an organic functional group.

The functional group of which oxygen is a part is preferably an ether, ester, or carbamate group. The functional group of which nitrogen is a part is preferably an amine, amide, or carbamate group. The functional group of which sulfur is a part is preferably a thiol, thio, sulfone (sulfinyl), or sulfoxide

(sulfonyl) group. The organic functional group of which carbon is a part is preferably an ester, carbamate or alkyl group.

Examples of compounds which may be used as the halopropynyl compound of this invention are especially the iodopropargyl (iodopropynyl) derivatives. In this regard, please see U.S. Pat. Nos. 3,923,870, 4,259,350, 4,592,773, 4,616,004, 4,719,227, and 4,945,109, the disclosures of which are herein incorporated by reference. These iodopropynyl derivatives include compounds derived from propargyl or iodopropargyl alcohols such as the esters, ethers, acetals, carbamates and carbonates and the iodopropargyl derivatives of pyrimidines, tiazolinones, tetrazoles, triazinones, sulfamides, benzothiazoles, ammonium salts, carboxamides, hydroxamates, and ureas. Preferred among these compounds is the halopropynyl carbamate, 3-iodo-2-propynyl butyl carbamate. This compound is included within the broadly useful class of compounds having the generic formulas:



wherein R is selected from the group consisting of hydrogen, substituted and unsubstituted alkyl, aryl, alkaryl, and aralkyl groups having from 1 to 20 carbon

atoms or from cycloalkyl and cycloalkenyl groups of 3 to 10 carbon atoms, and m and n are independently integers from 1 to 3, *i.e.*, not necessarily the same.

Suitable R substituents include alkyls such as methyl, ethyl, propyl, n-butyl, t-butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, dodecyl, octadecyl, cycloalkyls such as cyclohexyl, aryls, alkaryls and aralkyls such as phenyl, benzyl, tolyl, cumyl, halogenated alkyls and aryls, such as chlorobutryl and chlorophenyl, and alkoxy aryls such as ethoxyphenyl and the like.

Especially preferred are such iodopropargyl carbamates as 3-iodo-2-propynyl propyl carbamate, 3-iodo-2-propynyl butyl carbamate, 3-iodo-2-propynyl hexyl carbamate, 3-iodo-2-propynyl cyclohexyl carbamate, 3-iodo-2-propynyl phenyl carbamate, and mixtures thereof.

Relative proportions of the halopropynyl compound and the zinc pyrithione in the composition can vary widely and an optimum proportion likely will be affected by the intended application and the particular compounds selected. In any event, it is expected that compositions containing as little as 1 part of the halopropynyl compound to 9 parts of the zinc pyrithione and conversely as little as 1 part of the zinc pyrithione to 9 parts of the halopropynyl compound will be useful. Typically, useful compositions will contain from 1:2 to 2:1 parts of the halopropynyl compound to the zinc pyrithione and more usually about 1:1 relative parts by weight.

In accordance with the invention, the combined constituents can be included in a final formulation for use in such end use applications as paints, coatings, stucco, concrete, stone, cementaceous surfaces, wood, caulking, sealants, textiles, and the like, in a broad range from about 0.05% to 4.0% by weight active concentration of biocide mixture. Such compositions can be prepared from highly concentrated compositions of the active ingredients by appropriate dilution. The optimum useful range is most often about 0.1% to 2.0% of the combined ingredients in the final formulations for such end use systems. With the use of such modified formulations in end use systems, it is possible to protect surfaces as well as other substrates for extended periods of time against growth from algae.

Compositions of the present invention will generally be formulated by mixing the two active ingredients in a selected proportion with a liquid vehicle for suspending the active components. The vehicle may contain a diluent, a wetting-agent and a suspending agent. Expected uses of the algaecidal compositions include protection of wood, paint, coatings, adhesives, paper, textiles, plastics, cardboard, lubricants, caulkings, and the like. An extensive list of potential industries and applications for the present invention can be found in U.S. Pat. No. 5,209,930 which is herein incorporated by reference. The synergistic combinations of the halopropynyl compound, particularly a halopropynyl carbamate, and the zinc pyrithione are preferably

formulated as liquid dispersions or wettable powders, but may be provided as other suitable product types which are desirable and most useful, provided that the synergistic algaecidal activity is not adversely affected. In this regard, the composition of the present invention can be provided as a ready-for-use concentrated product in the form of aqueous and non-aqueous dispersions, powders, wettable powders, granulates, pastes, and the like.

When preparing formulations of the present invention for specific applications, the composition also will likely be provided with other adjuvants conventionally employed in compositions intended for such applications such as organic binding agents, additional algaecides, auxiliary solvents, processing additives, fixatives, plasticizers, UV-stabilizers or stability enhancers, water soluble or water insoluble dyes, color pigments, siccatives, corrosion inhibitors, antisettlement agents, anti-skinning agents and the like.

According to the present invention, substrates are protected from infestation by an algael organism simply by treating said substrate with a composition of the present invention. Such treating may involve mixing the composition with the substrate, coating or otherwise contacting the substrate with the composition.

The present invention is directed to synergistic mixtures of zinc pyrithione and a halopropynyl compound. A synergistic effect is generally regarded as the response of a mixture of two or more components that is greater than the sum of the separate responses of the

individual components. A mathematical approach for assessing synergy, as reported by F.C. Kull, P.C. Elisman, H.D. Sylwestrowicz and P.K. Mayer, in *Applied Microbiology*, 9:538 (1961) can be applied to binary mixtures using the following equation:

$$\text{Synergistic Index (SI)} = Q_a/Q_A + Q_b/Q_B$$

where:

Q_a = the quantity of component A used in a binary mixture that gives the desired effect (such as no bacterial growth),

Q_A = the quantity of component A which when used alone gives the desired effect,

Q_b = the quantity of component B used in a binary mixture that gives the desired effect, and

Q_B = the quantity of component B which when used alone gives the desired effect.

If the SI for a composition is less than one (<1), that composition exhibits synergistic behavior.

The following examples are presented to illustrate and explain the invention. Unless otherwise indicated, all references to parts and percentages throughout the application are based on weight.

EXAMPLES

Example 1

The compositions of the invention were found to be effective against algae. Specifically, algae which may be inhibited include without limitation, *Stichococcus basillaris*, *Chlorella vulgaris*, *Chlorella vulgaris* var. *viridis*, and *Trentepohlia aurea*. The preferred

combination of compounds, including IPBC and zinc pyrithione were tested in a weight ratio of 1:1.

In the test, an algae inoculum was prepared by washing a one-week old plate of each species into 100 ml isotonic water. The algaecidally active formulations were applied to a piece of filter paper at a rate of 225 g/m^2. After a drying time of one week, 1.26 cm^2 discs were cut from the filter paper and each one was placed on an agar plate. A suspension of algae (0.5 ml) was spread over the plate and the test filter paper disc with an appropriate spatula. The algae mixture used included *Stichococcus basillaris, Chlorella Vulgaris,Chlorella Vulgaris* var. *viridis* and *Trentepohlia aurea*.

The test plates were incubated at 15°C and evaluated after 2 weeks.

Table 1 shows the results of the tests which were carried out as described above. Test results actually show that unexpected synergistic results in inhibition and growth reduction were obtained with the tested mixtures of IPBC and zinc pyrithione as compared with effects obtained from the individual components when tested against algae. Number grades were given to those tests wherein the algae actually invaded the test filter paper discs.

Table 1

Biocide Concentration	0.05%	0.1%	0.2%	1.0%	1.75 %
Zinc Pyrithione	5	0	Z2	-	-
3-Iodo-2-Propynyl Butyl Carbamate	5	4	3	2	Z2
Zinc Pyrithione/3-iodo-2-Propyny Butyl Carbamate (1/1 weight ratio)	3	0	Z4	-	-

Z=Zone of Inhibition, the number following "Z" is the zone of inhibition in mm.

0=No growth
1=Trace Growth
2=Light Growth
3=Moderate Growth
4=Heavy Growth
5=Very Heavy Growth

Synergism calculated for the test carried out:

Level of 3-Iodo-2-Propynyl Butyl Carbamate in the effective combination (0.05%)/Passing level of 3-Iodo-2-propynyl Butyl Carbamate alone (1.75%)

+

Level of Zinc Pyrithione in the effective combination (0.05%)/Passing level of Zinc Pyrithione alone (0.1%)

or:

0.05/1.75 +0.05/0.1=0.52

Example 2

Table 2

WETTABLE POWDER

Component A	Parts/ Wt	Component B	Parts/Wt
3-iodo-2-propynyl butyl carbamate (IPBC)	50.0	Zinc Pyrithione	50.0
Silicon dioxide (silica)	5.0	Silicon dioxide (silica)	5.0
Aluminum-Silicate (Clay)	38.3	Aluminum-Silicate (clay)	38.3
Sulphonated Napthalene Condensate (Dispersant)	6.0	Sulphonated Napthalene Condensate (Dispersant)	6.0
Alkylated Napthalene Sulphonate (Dispersant)	0.7	Alkylated Napthalene Sulphonate (Dispersant)	0.7
TOTAL	100	TOTAL	100

The above compositions are prepared in equipment suitable for solids blending/grinding. Combinations of Component A and B are then added to paint, for example either separately or conjointly using a blender, at a ratio and percentage appropriate to achieve the desired inhibiting effect against algae.

Example 3

Table 3

DISPERSION

Component A	Part/Wt.	Component B	Part/Wt.
Propylene glycol	7	Propylene glycol	7
3-iodo-2-propynyl butyl carbamate (IPBC)	40	Zinc 2-pyridinethiol-1-Oxide (Zinc Pyrithione)	40
Aerosil (Hydrophobic Silica)	1	Aerosil (Hydrophobic Silica)	1
Mix			
Dispersant (Nonylethoxylate)	2.0		2.0
Wetting Agent (Ethoxylated Sulphate)	2.0	Wetting Agent (Ethoxylated Sulphate)	2.0
Thickener/Suspending Agent	1.0	Thickener/Suspending Agent	1.0
Water q.s.	100	Water q.s.	100

The above compositions are prepared in suitable processing equipment (*e.g.*, high speed disperser). Combinations of components A and B are added to paint, for example either separately or conjointly using a blender, at a ratio and percentage appropriate to achieve the desired inhibiting effect against algae.

While certain specific embodiments of the invention have been described with particularity herein, it will be recognized that various modifications thereof will occur to those skilled in the art and it is to be understood that such modifications and variations are to be included within the preview of this application and the spirit and scope of the appended claims.

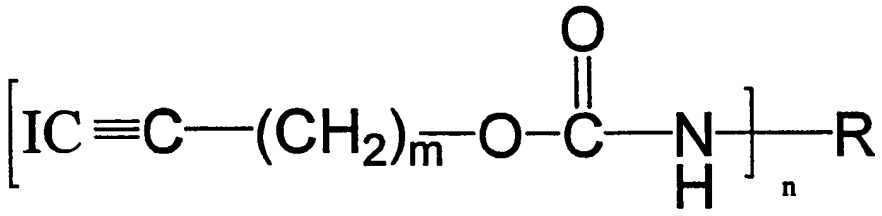
CLAIMS

We claim:

1. A algaecidal composition comprising a mixture of a halopropynyl compound and zinc pyrithione.

2. The composition of claim 1 wherein the halopropynyl compound is an iodopropargyl derivative selected from an iodopropargyl ester, an iodopropargyl ether, an iodopropargyl acetal, an iodopropargyl carbamate and an iodopropargyl carbonate.

3. The composition of claim 2 wherein the halopropynyl compound is an iodopropargyl carbamate of the formula:



wherein R is selected from the group consisting of hydrogen, substituted and unsubstituted alkyl, aryl, alkylaryl, and aralkyl groups having from 1 to 20 carbon atoms and cycloalkyl and cycloalkenyl groups of 3 to 10 carbon atoms, and m and n are independent integers from 1 to 3.

4. The composition of claim 3 wherein the iodopropargyl carbamate is 3-iodo-2-propynylbutyl carbamate.

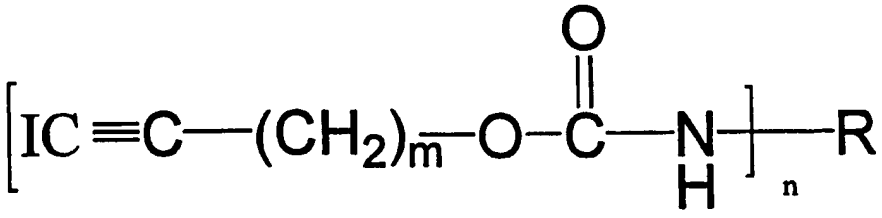
5. The composition of claim 4 wherein the halopropynyl compound and zinc pyrithione are present in a proportion of from about 1 part halopropynyl compound to 9 parts zinc pyrithione to about 9 parts halopropynyl compound to 1 part zinc pyrithione.

6. The composition of claim 1 containing from about 0.05% to 4.0% by weight of the mixture of said halopropynyl compound and said zinc pyrithione.

7. An algaecidal composition comprising a dispersion of a mixture of a halopropynyl compound and zinc pyrithione in a liquid vehicle.

8. The composition of claim 7 wherein the halopropynyl compound is an iodopropargyl derivative selected from an iodopropargyl ester, an iodopropargyl ether, an iodopropargyl acetal, an iodopropargyl carbamate and an iodopropargyl carbonate.

9. The composition of claim 8 wherein the halopropynyl compound is an iodopropargyl carbamate of the formula:



wherein R is selected from the group consisting of hydrogen, substituted and unsubstituted alkyl, aryl, alkylaryl, and aralkyl groups having from 1 to 20 carbon

atoms and cycloalkyl and cycloalkenyl groups of 3 to 10 carbon atoms, and m and n are independent integers from 1 to 3.

10. The composition of claim 9 wherein the iodopropargyl carbamate is 3-iodo-2-propynylbutyl carbamate.

11. The composition of claim 10 wherein the halopropynyl compound and zinc pyrithione are present in a proportion of from about 1 part halopropynyl compound to 9 parts zinc pyrithione to about 9 parts halopropynyl compound to 1 part zinc pyrithione.

12. A method of preparing the composition of /claim 7 comprising mixing said halopropynyl compound and said zinc pyrithione in a liquid vehicle.

13. A method for protecting a substrate from algael infestation comprising treating said substrate with an effective amount of the composition of claim 1.

14. A method for protecting a substrate from algael infestation comprising treating said substrate with an effective amount of the composition of claim 3.

15. A method for protecting a substrate from algael infestation comprising treating said substrate with an effective amount of the composition of claim 5.

16. A method for protecting a substrate from algael infestation comprising treating said substrate with an effective amount of the composition of claim 7.

17. A method for protecting a substrate from algael infestation comprising treating said substrate with an effective amount of the composition of claim 9.

18. A method for protecting a substrate from algael infestation comprising treating said substrate with an effective amount of the composition of claim 11.

19. A coating compositon comprising a mixture of a halopropynyl compound and zinc pyrithione, an organic binder and a liquid vehicle.

20. The coating composition of claim 19 wherein the halopropynyl compound and zinc pyrithione are present in a proportion of from about 1 part halopropynyl compound to 9 parts zinc pyrithione to about 9 parts halopropynyl compound to 1 part zinc pyrithione.

INTERNATIONAL SEARCH REPORT

Inte. ional Application No
PCT/US 97/21219

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A01N47/12

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 464 622 A (ROHM AND HAAS COMPANY) 7 November 1995 *see the whole document* ---	1-20
X	CHEMICAL ABSTRACTS, vol. 122, no. 11, 1995 Columbus, Ohio, US; abstract no. 125921v, FUKUDA ET AL.: "Antifungal mixtures for industrial goods" XP002057543 see abstract & JP 06 183 914 A --- -/--	1-20

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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1

Date of the actual completion of the international search	Date of mailing of the international search report
3 March 1998	17/03/1998

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INTERNATIONAL SEARCH REPORT

Inte .onal Application No
PCT/US 97/21219

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	CHEMICAL ABSTRACTS, vol. 122, no. 20, 1995 Columbus, Ohio, US; abstract no. 242251n, HIRAIWA ET AL.: "Mold-resistant and waterproof fabrics and their manufacture" XP002057544 see abstract & JP 06 313 269 A	1-18

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Information on patent family members

Inte. onal Application No
PCT/US 97/21219

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		CN 1062448 A	08-07-92
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